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Zero field tensor for Ni(II) in Zn (ethylenediamine)₃ (NO₃)₂: EPR study

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Single crystal EPR of Ni(en)₃²⁺ (en = ethylenediamine) doped in Zn(en)₃(NO₃)₂ is reported. Our results based on exact diagonalization procedure indicate that the Ni(en)₃²⁺ units undergo distortion along the threefold axis which coincides with the crystallographic *c* axis. The zero field tensor is found to be axially symmetric with *D* being $0.831 \pm 0.006 \text{ cm}^{-1}$. The utility of *S* = 1 ions in obtaining information regarding molecular distortions is also evidenced.

INTRODUCTION

Electron paramagnetic resonance of transition ions like Cu²⁺ and Mn²⁺ has been extensively carried out in ethylenediamine complexes of Cd²⁺ and Zn²⁺.^{1,2} In these complexes Cu²⁺ has been studied to understand the possible Jahn–Teller effects and Mn²⁺ to understand the ligand field symmetry. The analysis of EPR spectra of Mn²⁺ ions in these lattices is quite difficult due to the fact that the zero field splitting is very small and there are many magnetically distinct sites leading to overlap of resonance features. Despite these difficulties, logical conclusions have been drawn regarding the molecular distortions based on single crystal EPR of Mn²⁺ in Zn (ethylenediamine)₃ (NO₃)₂ by Sastry *et al.*³ Our own motivation is that EPR of Ni²⁺ (orbitally singlet ground state) substitutionally incorporated for Zn²⁺ would be worthwhile to study for the following reasons: (a) While Mn²⁺ gives 30 lines (in cases *D* ≠ 0) for each magnetically distinct site, Ni²⁺ gives two lines only (*S* = 1: nuclear hyperfine interaction is absent for Ni, *I* = 0, 98.8%). (b) The zero field splitting is generally large for Ni²⁺ complexes. The large separation between the resonance lines is useful in the unambiguous analysis of the site symmetry. (c) Ethylenediamine complexes are conformationally labile⁴ and the EPR studies of Cu²⁺ and Mn²⁺ failed to reflect the existence of conformational isomers at ambient temperatures in Zn(en)₃(NO₃)₂ due to fast interconversion among the isomers compared with the anisotropies involved in these experiments like the Cu²⁺ *g* anisotropy, hyperfine anisotropy, and the zero field splitting for Mn²⁺. However, at low temperature the presence of six magnetically distinct sites with orthorhombic zero field tensor for Mn(II) in Zn(en)₃(NO₃)₂ has led the authors³ to conclude that one of the conformational isomers ($\delta\lambda\lambda$ or $\delta\delta\lambda$ conformer) is favored. They have also pointed out that the fast interconversion among the isomers is leading to nearly axial crystal field at ambient temperatures. This implies that the molecular structure provided by x-ray data is likely to be the “average” structure of the conformers. So, it is interesting to carry out the EPR study of Ni²⁺ which is expected to have higher zero field splitting and see whether the conformational isomers could be detected at ambient temperatures.

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With these points in view we have carried out EPR study of Ni²⁺ in Zn(en)₃(NO₃)₂. It should also be mentioned that the large *D* value for Ni²⁺ necessitates measurements at higher frequencies and it is likely that perturbation approaches will not yield satisfactory results.

EXPERIMENTAL

Single crystals of Ni²⁺ doped Zn(en)₃(NO₃)₂ were grown by slow evaporation of an aqueous solution containing Zn(NO₃)₂ and ethylenediamine in the molar ratio 1:3. Ni²⁺ in the form of Ni(NO₃)₂ was incorporated to about 2 to 5 mol %. Very good single crystals with hexagonal morphology were obtained within a few days. The morphological characteristics of doped crystals are identical with those of the host crystals. The crystal morphology was determined on Enraf–Nonius CAD-4 x-ray diffractometer. The morphology of single crystals was found to be as shown in Fig. 1. Rotations were done along the crystallographic *c* axis, an axis perpendicular to (110) plane, and along an axis perpendicular to these two. The rotation axes are hereafter referred as *c* axis, axis II, and axis III, respectively. All measurements were carried out at ambient temperatures.

Crystal structure of Zn(en)₃(NO₃)₂

The crystal structure of Zn(en)₃(NO₃)₂ is known⁵ to be isomorphous with Ni(en)₃(NO₃)₂⁶ which crystallizes in

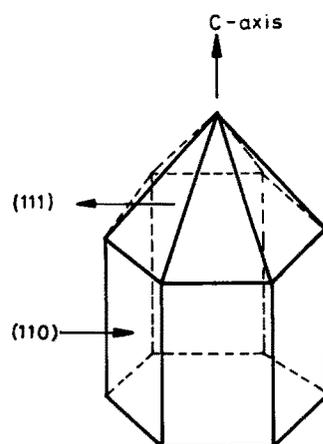


FIG. 1. Morphology of single crystals of Ni²⁺ doped Zn(en)₃(NO₃)₂.

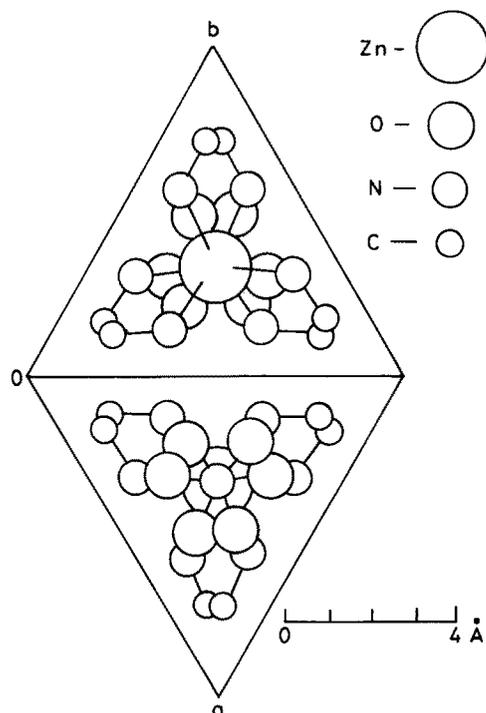


FIG. 2. Projection of the unit cell of $\text{Zn}(\text{en})_3(\text{NO}_3)_2$ along the crystallographic c axis (taken from Ref. 6).

hexagonal $P6_322$ (D_3^d) space group. The unit cell dimensions are $a = b = 8.87 \text{ \AA}$ and $c = 11.41 \text{ \AA}$. The projection of the unit cell along the crystallographic c axis is shown in Fig. 2. From the projection it could be realized that the $\text{Zn}(\text{en})_3^{2+}$ units have threefold symmetry axis along the crystallographic c axis and the local point symmetry is D_3-32 . The two $\text{Zn}(\text{en})_3^{2+}$ moieties in the unit cell are related by twofold symmetry and are located at $(1/3, 2/3, 3/4)$ and $(2/3, 1/3, 1/4)$.

RESULTS AND DISCUSSION

At certain orientations the observed resonances at X -band frequency fall in the range of the spectrometer, which is 0–7000 G. However, at certain other orientations the resonances are beyond the X -band magnetic field range. It was obvious therefore that the zero field splitting is quite high and it is of the order of (or greater than) the X -band microwave quantum (0.32 cm^{-1}).

Measurements were therefore carried out at Q -band frequency. For rotation about the crystallographic c axis, it was observed that there are two high intensity lines. The two lines are consistent with the $S = 1$ system. Apart from these two lines there are a few lines due to Mn^{2+} impurity and a weak three line pattern due to Cr^{3+} impurity. However, the two high intensity lines do not show any variation in resonance field position with rotation angle. This clearly reveals that we are dealing with an axially symmetric zero field tensor with the unique axis along the crystallographic c axis.

When the crystal is rotated along axis II or axis III, these two resonances show variation in field position with rotation angle and the observed variation is characteristic of $S = 1$ ion. The anisotropy for rotation about axis II is identical with that for axis III. This clearly confirms that the D_{zz} is parallel to the c axis. Some of the spectra for rotation about axis II are shown in Fig. 3. It can be seen from the spectrum at $\theta = 0$, that the low field line is much less intense compared with the high field line indicating that D is positive for this system.

Now that the direction D_{zz} of the axially symmetric zero field tensor is clearly established, the next problem is to establish the principal values. It could be easily realized that the perturbation approach in this situation does not yield correct values, as can be judged by the fact that along an axis perpendicular to the crystallographic c axis the separation

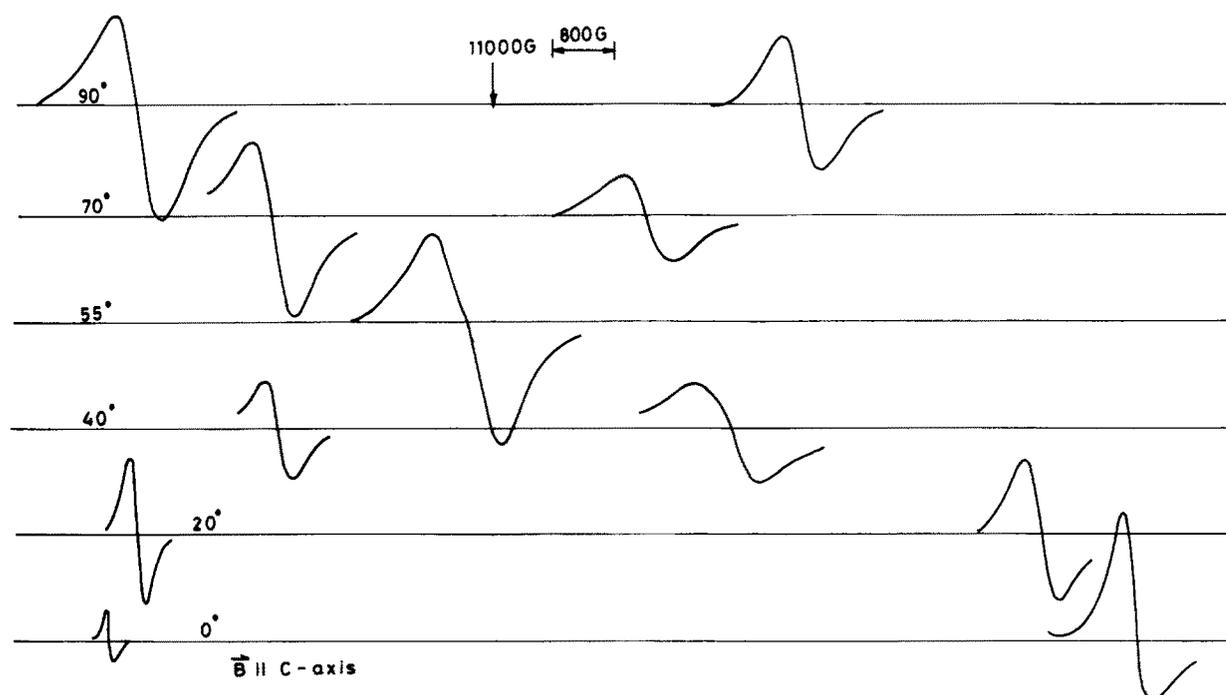


FIG. 3. Single crystal EPR spectra of Ni^{2+} doped $\text{Zn}(\text{en})_3(\text{NO}_3)_2$ for rotation about axis II.

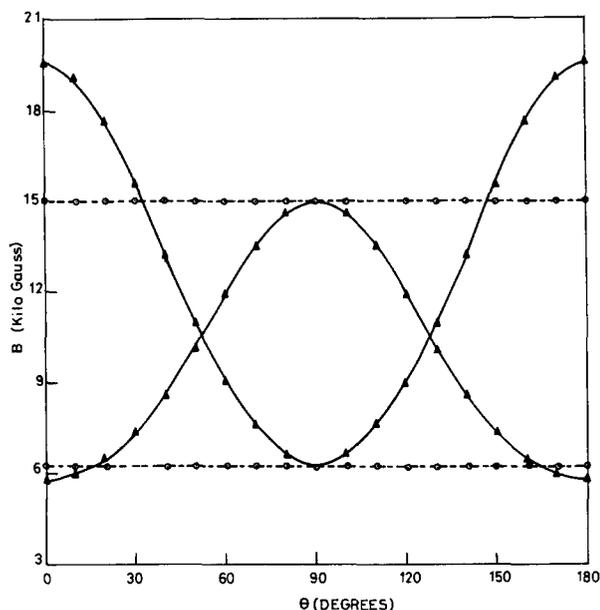


FIG. 4. Angular variation of fine structure resonances. Continuous and dashed lines are simulated variations for rotations about axis II and c axis, respectively. \blacktriangle and \odot are experimental points. For rotation about axis II $\theta = 0$ corresponds to magnetic field being parallel to the crystallographic c axis.

between the two lines is not approximately half that observed for magnetic field parallel to the c axis. Hence, the exact diagonalization procedure developed by Kopp⁷ was used. An additional problem that was encountered is that in such cases g and D cannot be directly measured from the spectra. Therefore, the "tetrahedral interpolation" procedure of Kopp was used with D_{zz} and g as variables. Nine orientations at 10° interval were taken and the values of D_{zz} and g were derived by best fit obtained by an interpolation. As pointed out by Kopp the procedure does not yield the same D_{zz} and g values for all the orientations. However, after repeated interpolations the best fit value for D_{zz} and g (turns out to be isotropic) were obtained. With these values the angular variation for rotation about c axis and axis II were simulated. The agreement is very good as can be seen in Fig. 4. The spin Hamiltonian parameters along with the direction cosines are given in Table I.

The two $\text{Ni}(\text{en})_3^{2+}$ moieties in the unit cell are not related by inversion symmetry. Hence, the observation of only one magnetically distinct site with D_{zz} direction being the crystallographic c axis, and the fact that the molecules in the unit cell have their threefold axes along the c axis could be rationalized in terms of distortion of the two molecules along the threefold axis. At room temperature exchange among the various possible conformers results in a time averaged

TABLE I. Spin-Hamiltonian parameters for Ni^{2+} doped $\text{Zn}(\text{en})_3(\text{NO}_3)_2$.

Parameter	Value (in cm^{-1})	Direction cosines a^*bc reference frame		
D_{zz}	0.554 ± 0.004	0	0	1
D_{xx}	-0.277 ± 0.004
D_{yy}	-0.277 ± 0.004
$g_{xx} = g_{yy} = g_{zz} = 2.200 \pm 0.006$				

spectrum. Despite the high magnitude of D , we could not observe the various conformers, most probably due to inter-conversion among isomers at frequencies higher than the magnitude of D . X -band spectra at 20 K do indicate the presence of many sites presumably due to the conformational isomers, but an exhaustive analysis of X -band spectra could not be carried out due to very high zero field splitting. Q -band spectra at low temperatures were not recorded due to lack of this facility.

CONCLUSIONS

The essential conclusions of this study are

- (1) The distortion of $\text{Ni}(\text{en})_3^{2+}$ octahedron is axial (E is exactly zero).
- (2) The c axis, which coincides with the threefold symmetry axis, is found to be the distortion axis.
- (3) The D value for $\text{Ni}(\text{en})_3^{2+}$ is evaluated to be $0.831 \pm 0.006 \text{ cm}^{-1}$.
- (4) Complete diagonalization of the spin-Hamiltonian matrix is able to produce results which gave a very good fit to the experimental observation.

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